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POLYMERIZATION OF STYRENE

BY

PERCHLORIC ACID

Final Technical Report

By

D.C. Pepper

October 1968

EUROPEAN RESEARCH OFFICE

United States Army

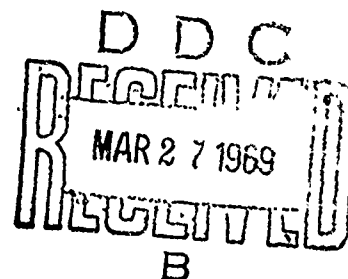
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### Summary

The report presents extensive measurements of (number average) molecular weights, yields and rates obtained in the polymerization of styrene by perchloric acid in solution in methylene chloride over the wide temperature range  $0^{\circ}\text{C} - -97^{\circ}\text{C}$ .

They show that the polymerization changes its kinetic pattern as the temperature is reduced and that the following well-defined characteristics can be recognised in different regions.

- (1) At  $-97^{\circ}$  a 'flash' polymerization, producing only a definitely limited yield of polymer, of  $\bar{M}_n$  corresponding to one chain per initiator, i.e. no transfer reactions are involved. The  $\bar{M}_n$  values obtainable are correspondingly limited and low ( $< 10,000$ ) but the distributions are very wide ( $\bar{M}_w/\bar{M}_n \sim 20$ ).
- (2) At intermediate temperatures, e.g.  $-78^{\circ}$  to  $-30^{\circ}$ , a two stage reaction of which Stage I is similar to the above, and is followed by Stage II, a stationary polymerization. Transfer reactions become appreciable but apart from this complication the polymerizations have the character of a living polymerization, i.e.  $\bar{M}_n$  increases with conversion and is inversely proportional to initiator concentration.
- (3) Above  $-30^{\circ}$  - a conventional transfer dominated stationary polymerization in which  $\bar{M}_n$  decreases with conversion and is virtually independent of initiator concentration.

An inert perchlorate salt  $n\text{Bu}_4\text{NClO}_4$  causes severe reduction of the Stage I yields and partial reduction of the Stage II rates, indicating that free carbonium ions are the main propagating species in Stage I and two species act in Stage II.

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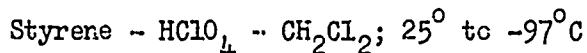
## 1. Objectives and Scope of this Report

### General Objective

Polymerization by the cationic mechanism has in principle a very wide relevance, because of the great number of susceptible monomers and the potentialities of flexible control through the different activities of the wide spectrum of initiators, the acids and Friedel Crafts catalysts. In practice the potentialities have not been extensively realised on the industrial scale (with the exception of isobutene - Butyl Rubber).

The short-term reason for this lack of success has been that empirical investigations have not found ways of overcoming the characteristic disadvantage of this class of polymerizations - that the polymers tend to have very low molecular weights. The deeper reason is that no satisfactory general theoretical framework yet exists which can describe the polymerizations in adequate detail. Thus it has not been possible to demonstrate (as distinct from infer) the cationic nature of the propagating species: the overall kinetic pattern is usually not known with any assurance, nor are the specific factors which limit the molecular weights.

The chief limitation on previous fundamental studies in this field has been that (usually for good experimental reasons) it has not been possible to obtain both rates and molecular weights over a sufficiently wide range of temperatures, and that any molecular weights obtained were usually not number average values, and hence were of limited use for kinetic deductions. The objective of the present research was therefore to obtain this type of data in the greatest possible detail over the widest temperature range, and to this purpose the system chosen was perhaps the most reproducible cationic polymerization



### Scope of this Report

Apart from a few results obtained with the related monomers  $\alpha$  Methyl styrene and 2:4:6 Trimethyl styrene, this report describes the yields, rates and molecular weights found in the styrene-perchloric acid polymerization between  $25^\circ$  and  $-97^\circ$  and leads to a virtually complete understanding of this system. It reveals the following novel features

- 1) A 'flash' polymerization at very low temperature
- 2) An 'intermittently living' polymerization at intermediate T ( $> -80^\circ$ ) becoming progressively less ideal (affected by transfer) as T rises
- 3) A demonstration (through a 'perchlorate salt effect') that free ionic species dominate the propagation in the 'flash' polymerization, and play a partial role at all temperatures.

## 2. Experimental Methods

Polymerization rates were measured, and polymer specimens obtained by a simple isolation method in which samples of the reacting mixture were blown at intervals from the reaction vessel into a 'killing solution'. The reaction vessel, a pyrex cylinder,  $\sim 35$  cm x 7 cm diameter, carried standard socket ports for the introduction of reagents, and for the mounting of a sample-expulsion tube, a thermistor well, and a central, 2 cm diameter, tube with a fragile bottom. In normal operation, monomer and solvent were placed in the reaction vessel, and catalyst solution in the central tube, these filling operations being conducted under dry-nitrogen counterflow. After the reagents had reached thermostat temperature, the catalyst vessel was broken by releasing a heavy glass breaker and the reagents mixed by rapid dry-nitrogen bubbling. The usual scale of experiment involved  $\sim 100$  ml of solutions: for this volume the estimated mixing time was  $\sim 1$  second.

Styrene and solvents were purified and dried, and anhydrous perchloric acid prepared by methods previously described.<sup>1</sup>

Weighed samples were collected in the 'killing solution' (aqueous methanol -  $\text{CH}_2\text{Cl}_2$ ), the solvents and monomer removed by steam distillation and the polymer filtered and dried to constant weight in a vacuum oven at  $\sim 40^\circ\text{C}$ . Samples for molecular weight determination were further purified by freeze-drying from benzene under high vacuum. Number average molecular weights were determined in benzene at  $25^\circ$  by vapour-pressure osmometry.

Except where otherwise stated, all polymerizations were carried out using the solvent, methylene chloride, and mostly in dilute solution, with styrene 5% by volume = 0.435 mole per litre.

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1. D.C. Pepper & P.J. Reilly, *Proc. Roy. Soc. A*, 291, 41 (1966)

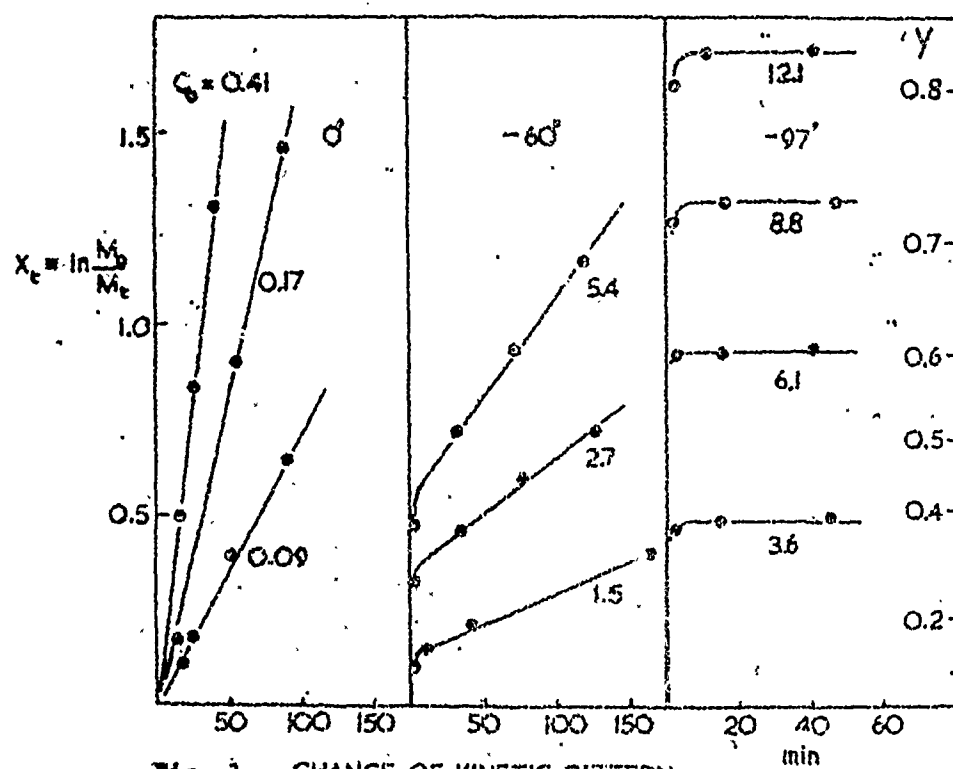


Fig. 1 CHANGE OF KINETIC PATTERN  
 $M=0.43$  at  $C_0$  shown (m)

### 3. Experimental Results

All results are collected in the Appendix in the form of tables which show for the various experimental conditions the following direct or derived information:

- (1) Percentage yield of polymer - or its fractional form  
 $Y = \Delta M/M_0$  where  $M = [\text{Styrene}]$
- (2) The derived first order integrated conversion function  $X$ ,  
 $X \equiv \ln(M_0/M_t) \equiv \ln(1 - Y)^{-1}$
- (3) The number average molecular weight of the sample,  $\bar{M}_n$
- (4) The derived degree of polymerization  $P_n \equiv \bar{M}_n/104$
- (5) The calculated number of polymer chains formed per initiator (C),  $n \equiv \Delta M/(C_0 \cdot \bar{P}_n) \equiv Y \cdot M_0/(C_0 \bar{P}_n)$

The empirical relationships indicated by the results are set out below, illustrated by appropriate figures, together with brief explanations, comments and interim deductions.

#### 3.1 Kinetic Patterns at Different Temperatures

Previous investigations of the polymerization of styrene by perchloric acid in ethylene dichloride<sup>1)</sup> and in methylene chloride<sup>2)</sup>, in the region of room temperature, have found very simple overall kinetics. Between 25°C and -30°C  $\text{HClO}_4$  induces a rate of polymerization, found to be accurately of the first order in [styrene], and zero order in  $[\text{HClO}_4]$  with the observed first order rate constant proportional to the initial concentration of the initiator  $[\text{HClO}_4]_0$ , i.e.

$$-dM/dt = k[\text{HClO}_4]_0 M_t$$

or in integrated form

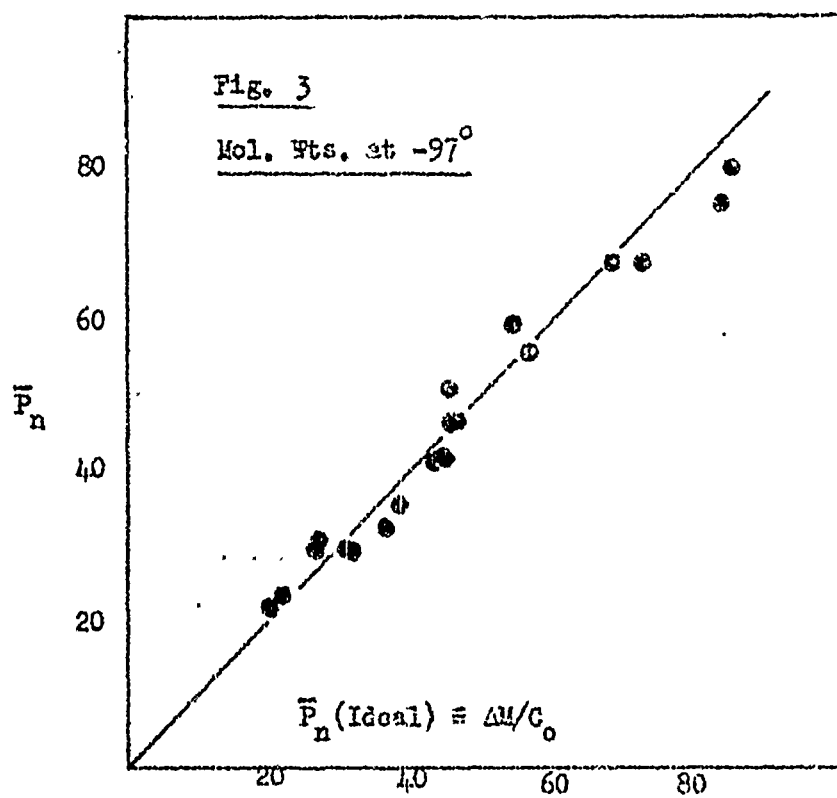
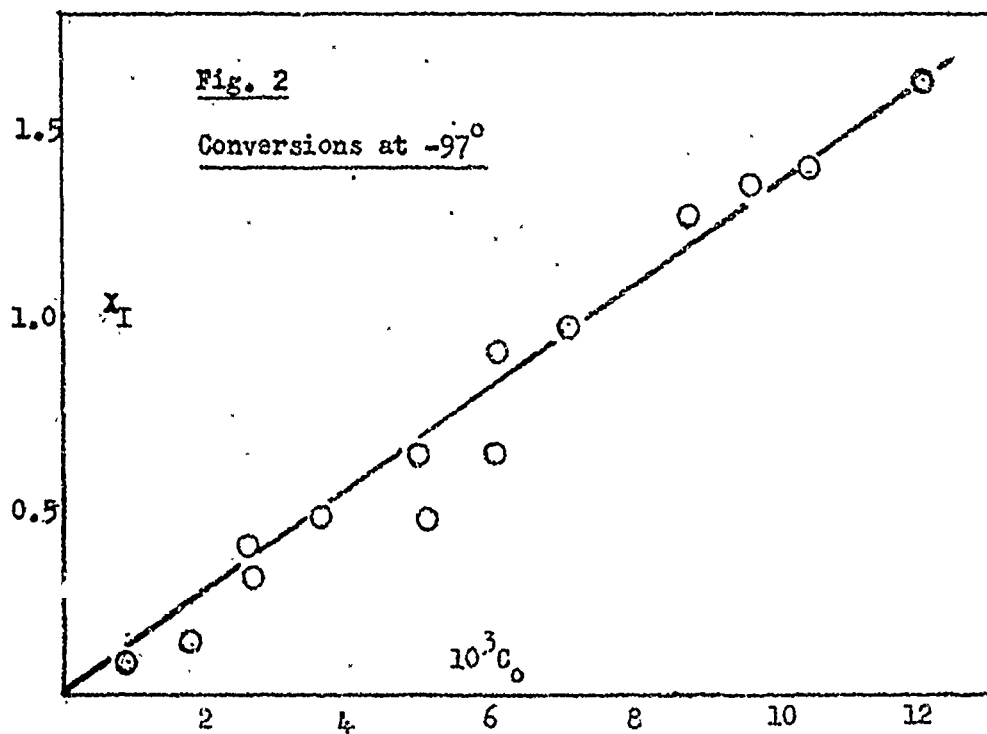
$$X_t \equiv \ln(M_0/M_t) = \ln(1 - Y_t)^{-1} = k[\text{HClO}_4]_0 \cdot t.$$

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1. D.C. Pepper & P.J. Reilly, Proc. Roy. Soc. A, 291, 41 (1966)

2. D.C. Pepper, Final report on DA 91 591 4217 Sept. 1967





Under these conditions there is no limitation to the yield; a given charge of perchloric acid causes 100% conversion of the monomer and continues to polymerise any subsequent additional charges of monomer indefinitely, i.e. the initiator is not consumed, or is regenerated.

Figure 1 illustrates this behaviour with plots of  $X-t$  at  $0^{\circ}\text{C}$  and compares it with similar plots for reactions at  $-60$  and  $-97^{\circ}\text{C}$ . It can be seen that a quite different kinetic pattern is found at  $-97^{\circ}$ , and that the behaviour at  $-60^{\circ}$  shows features of both patterns.

The characteristic behaviour at  $-97^{\circ}$  is clearly that a given charge of  $\text{HClO}_4$  now produces not a continuous rate but a definitely limited yield, formed very rapidly ( $< 1^i$ ), and thereafter independent of time. As shown in the next section, the conversion function  $X$  is found proportional to  $[\text{HClO}_4]_0$ , i.e. the yield itself rises with  $[\text{HClO}_4]_0$  but approaches 100% only asymptotically.

The effect of reaction temperature on molecular weights shows a converse trend, from a complex pattern at room temperature to a very simple one at  $-97^{\circ}$ . The detailed results are therefore best presented in a sequence starting with those at the lowest reaction temperatures.

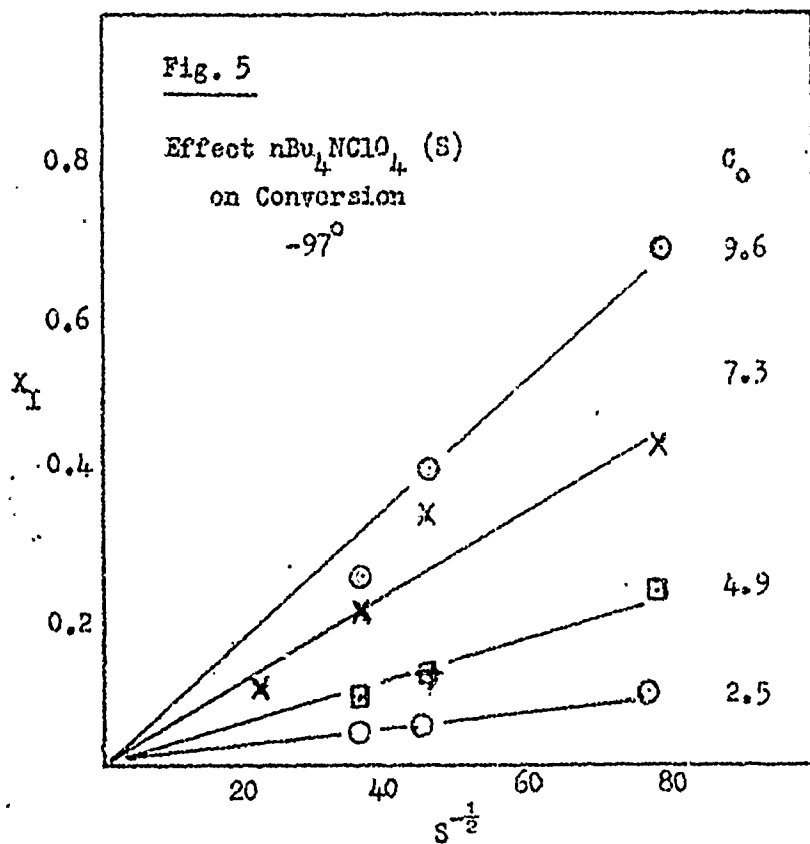
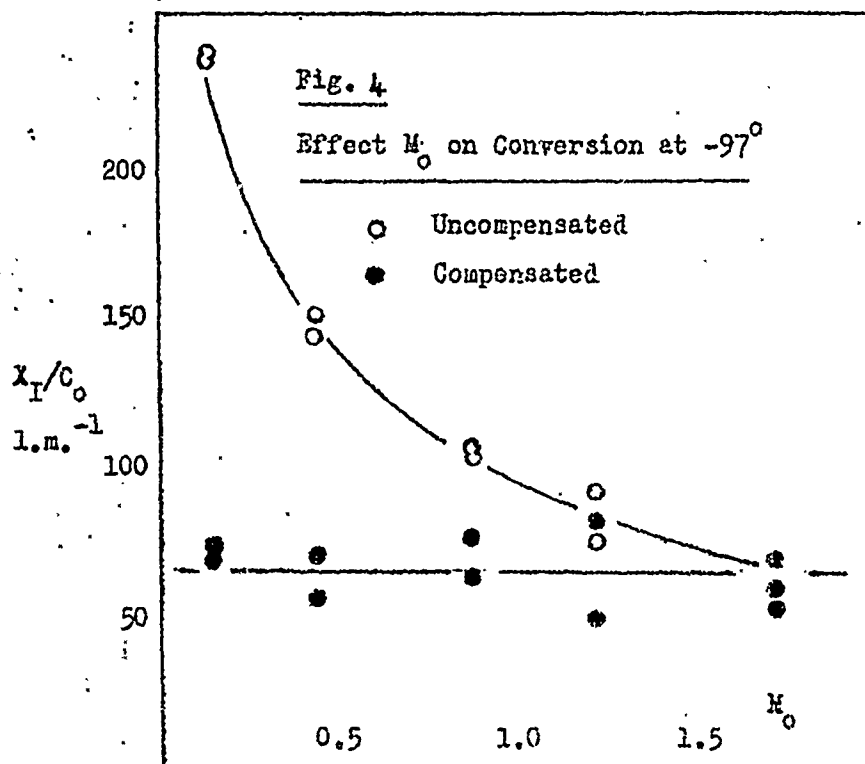
### 3.2 Results at $-97^{\circ}\text{C}$

#### 3.2.1 Effect of $[\text{HClO}_4]_0$ on Conversion at $-97^{\circ}$

The detailed results collected in Table J show that (at a given initial monomer concentration,  $M_0 = 0.455$ ) the yields increase with, but are not proportional to the initiator concentration. The integrated first order conversion function,  $X$ , is however proportional to  $[\text{HClO}_4]_0$  as demonstrated by Fig. 2. The mean value derived for the proportionality constant (in  $X = k'C_0$ ) is

$$k' = 137 \text{ L.m}^{-1} \text{ at } -97^{\circ}\text{C} \quad \dots \dots \dots (1)$$

A group of earlier measurements (Expts D 107-110) had given higher values of  $k'$  ranging between 172 and 215. The reason for the discrepancy is not known, but the lower value 137 is preferred as being more reliable and consistent with those found at other monomer concentrations (para. 3.2.3, Table II).



### 3.2.2 Effect of $[\text{HClO}_4]_0$ on Molecular Weight at $-97^\circ\text{C}$

The number average molecular weights fall with increasing initiator concentration in such a manner that each initiator molecule forms only one polymer chain. As col. (8) of Table I indicates,  $n$  ( $\equiv Y.M_0/C_0.\bar{P}_n$ ) is close to unity in all cases, i.e. the degree of polymerization  $\bar{P}_n$  has the "ideal" value  $Y.M_0/C_0$ . The validity of this general relationship is also demonstrated by a plot of  $\bar{P}_n$  against  $\bar{P}_n$  (ideal) in Fig. 3. Since the yield is itself related to  $C_0$  by equation (1), the overall equation relating molecular weight to initiator concentration is, at  $-97^\circ\text{C}$

$$\bar{M}_n \equiv 104 \bar{P}_n = 104.(M_0/C_0) \left\{ 1 - \exp(-137 C_0) \right\} \dots \dots (2)$$

In equation (2) the function in  $C_0$  has the form that tends, in the limit, to the value of the constant as  $C_0 \rightarrow 0$ . Hence the results of Table I indicate the very interesting and unexpected conclusion that the polymer formed in such a 'flash' polymerization can have only a definitely limited maximum degree of polymerization given by

$$\bar{P}_n (\text{lim}) = k'.M_0 \quad (k' \text{ of equation (1)} \dots \dots (3)$$

For the experimental conditions of Table I

$$\bar{M}_n (\text{lim}) \equiv 104 \bar{P}_n = 6200$$

### 3.2.3 The effect of $M_c$ at $-97^\circ\text{C}$

The solvent  $\text{CH}_2\text{Cl}_2$  is much more polar ( $\epsilon \sim 17$  at  $-97^\circ$ ) than styrene ( $\epsilon \sim 3$ ). Consequently a simple variation of monomer concentration introduces also a change in the polarity of the reaction medium, which is usually found to influence the rate constants in ionic polymerizations. The experiments recorded in Table II therefore compare the results of a simple variation of  $M_0$  (columns 4 and 6) with results in 'dielectrically compensated' solutions (cols. 5 and 7). In the latter the polarity is kept approximately constant at the value corresponding to 20% styrene; 80%  $\text{CH}_2\text{Cl}_2$ , i.e. the various

Fig. 6 Stage I Conversions

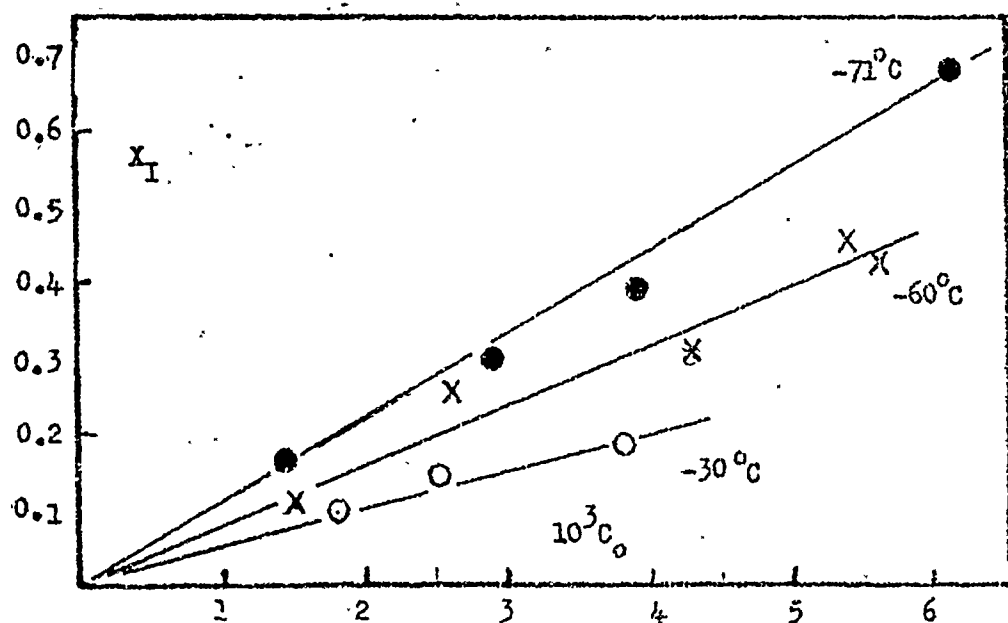
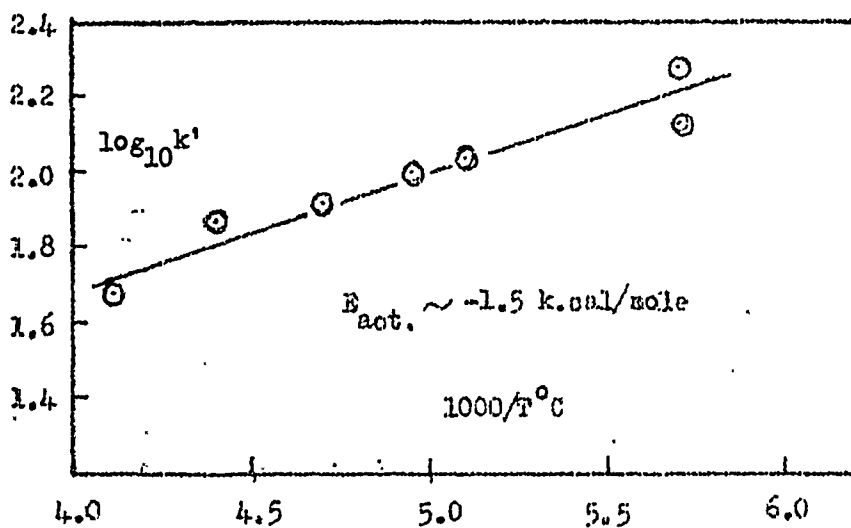


Fig. 7 T Dependence of Stage I Conversions



solutions contained  $x\%$  styrene,  $(20 - x)\%$   $\text{CCl}_4$  and  $80\%$   $\text{CH}_2\text{Cl}_2$  by volume. The solvent  $\text{CCl}_4$  has previously been found to be a satisfactory compensator at room temperature<sup>1</sup>.

It can be seen from Table II and Fig. 4 that the yields and conversion constants,  $k' (\equiv X/C_0)$ , fall with increasing monomer concentration in uncompensated solutions. In the 'compensated' solutions no trend is found, and it can be concluded that the conversion constant  $k'$  is a true rate constant (or function of rate constants) and has no explicit dependence on  $M_0$ , though it does decrease with the decreases in polarity of the system consequent on increases in the proportion of the non-polar monomer present.

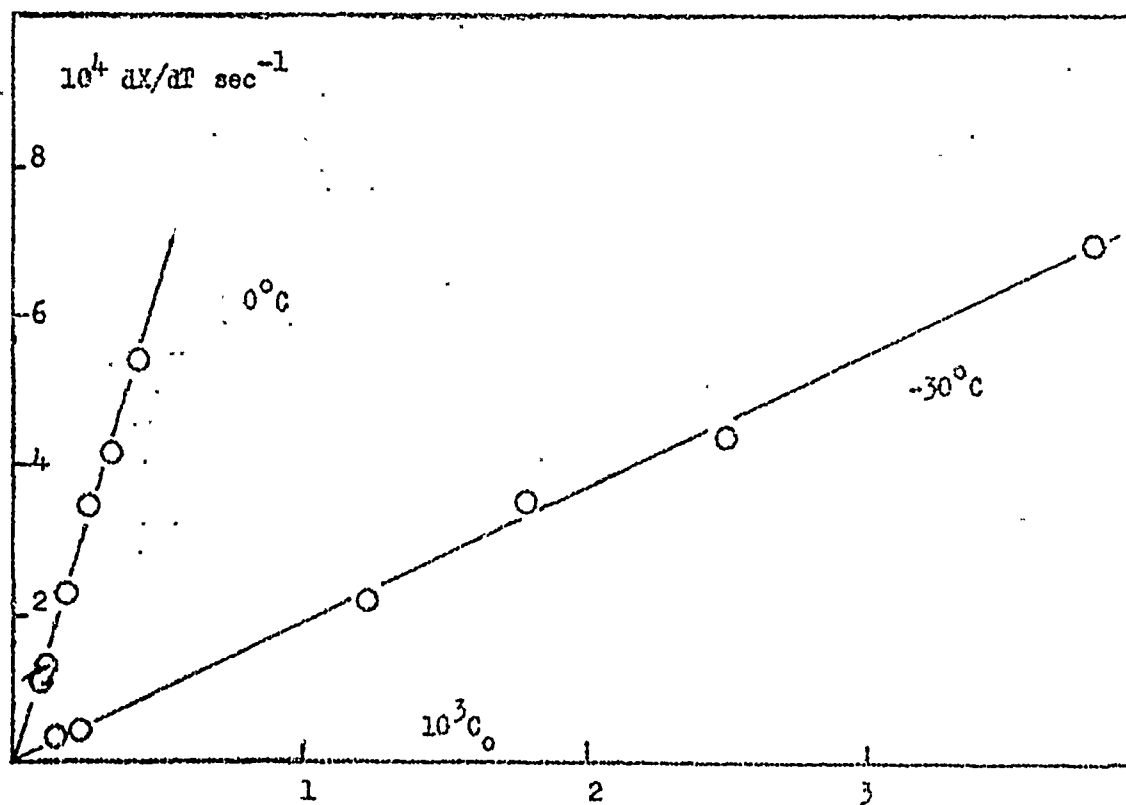
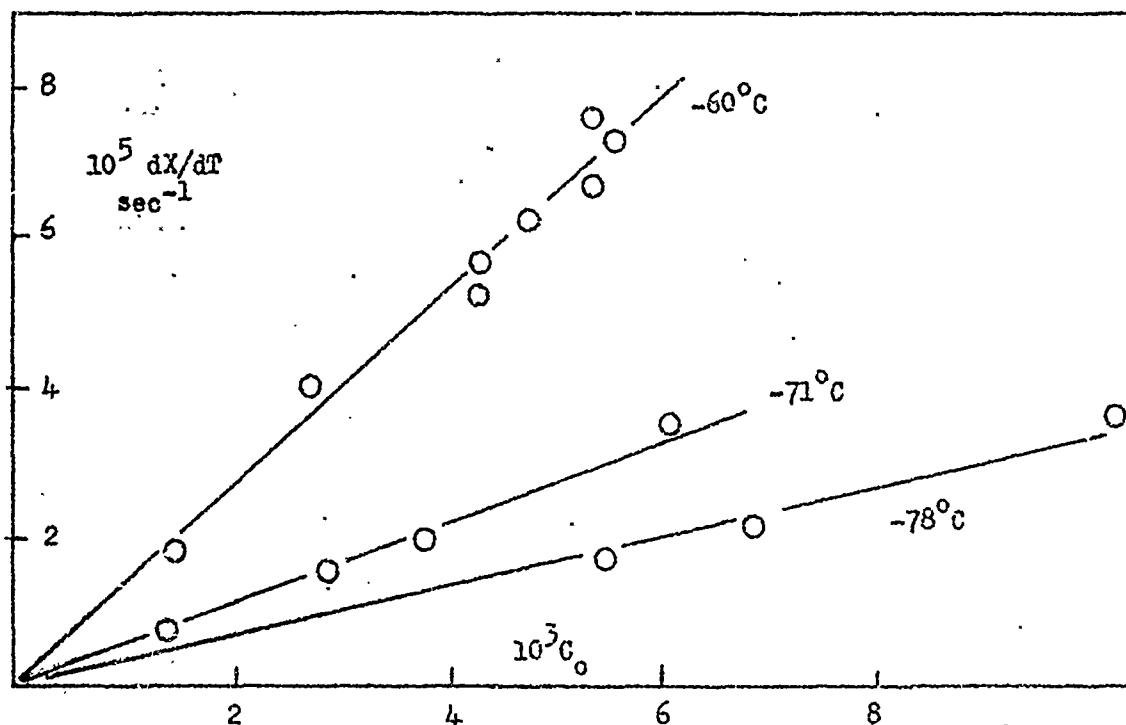
Columns 8 and 9 of Table II show that while the molecular weights from uncompensated and compensated solutions are different, the differences arise simply from the differences in yields, and that  $n$ , the number of chains per initiator, remains unity in all cases. Fig. 3, which illustrates this conclusion, contains points corresponding to both compensated and uncompensated systems.

#### 3.2.4 Effect of Tetra n-butyl Ammonium Perchlorate at $-97^\circ\text{C}$

To test whether the very rapid 'flash' polymerization at  $-97^\circ$  was propagated by free carbonium ions, an investigation was made of the effect (on yield and molecular weight) of the salt,  $\text{nBu}_4\text{NClO}_4$ . This salt is sufficiently ionized in  $\text{CH}_2\text{Cl}_2$  at  $-97^\circ$  ( $K_a \approx 7 \times 10^{-4}$ ) to provide free  $\text{ClO}_4^-$  anions in concentrations expected to cause appreciable suppression of the ionization of polymer perchlorate.

As can be seen from the results in Table III very small concentrations of this salt ( $< \text{millimolar}$ ) cause progressive reduction of the yield and the molecular weight of polymer. Quantitatively, as shown by Fig. 5, the conversion function  $\bar{X}$ , is proportional to the reciprocal of the square root of the salt concentration, implying zero conversion at infinite salt concentration. Hence the results lead to the conclusion that there is virtually no non-suppressible contribution to the polymerization rate, i.e. that under these conditions the polymerization is propagated predominantly by free carbonium ions.

Fig. 8 Stage II First Order Constant-dependence on  $C_0$



The values of  $\bar{M}_n$  are lowered, but not to an extent expected from the reduction in yield, if equation (20) of para. 3.2.2 were still valid. In fact, as shown by col. 7, Table III, the number of chains formed per catalyst falls with increasing salt concentration, implying progressively less complete utilisation of the initiator. There could be several reasons for this effect, which will be discussed later.

### 3.3 Results at Intermediate Temperatures ( $-77^\circ$ - $-30^\circ$ )

As previously illustrated for  $-60^\circ\text{C}$  in Fig. 1 the typical behaviour in this region is that the polymerization shows an initial 'burst' of reaction, followed by a slow and slowly declining rate. The integrated first order conversion function  $X$  is found to increase linearly with time in the second stage (Stage II). Back extrapolation to  $t = 0$  permits evaluation of the conversion  $X_I$  produced by Stage I. As the reaction temperature is raised, the Stage I conversions diminish, and the Stage II rate constants  $dX/dt$  rise until at  $T \gtrsim -30$  no Stage I can be discerned. The following sections describe the effect of initiator and perchlorate salt concentration on the conversion in the two stages.

#### 3.3.1 Stage I Conversions

Figure 6 shows the effect of initiator concentration at  $-71^\circ$ ,  $-60^\circ$  and  $-30^\circ$ . Over the range of concentrations examined the conversions are best described by a simple proportionality, as found for the total conversions at  $-97$  (Fig. 2). The values of the proportionality constant,  $k'$ , are collected in Table X, and shown as an Arrhenius plot in Fig. 7. There is appreciable quantitative uncertainty in some of the values (e.g. between 137 and 190 at  $-97$ ), but in general they show a mutually consistent trend with temperature corresponding to a small (apparently negative), i.e. composite activation energy  $E_{\text{act}} \sim -1500$  k.cal/mole.



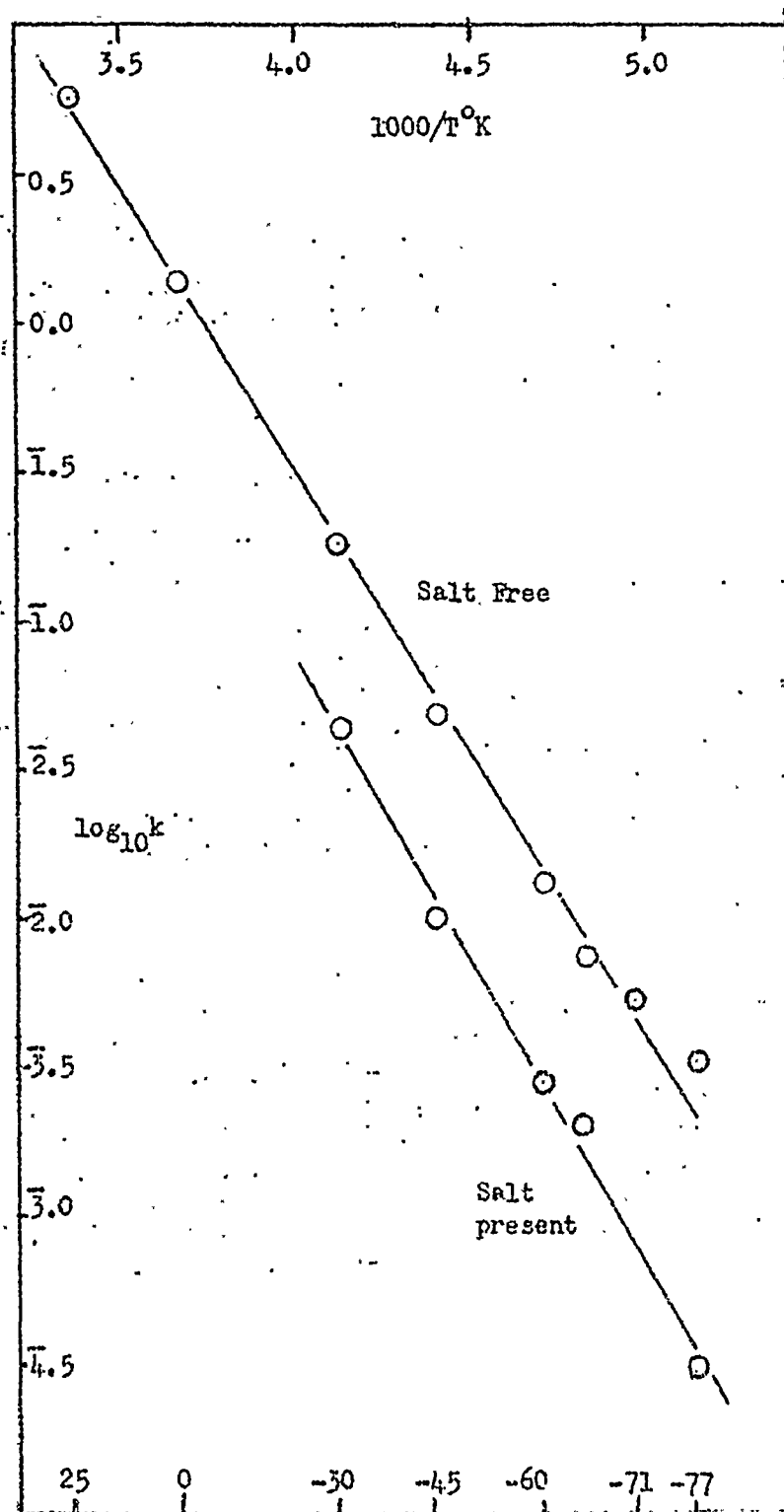


Fig. 9 Temperature dependence of Stage II rate constants

### 3.3.2 Stage II Rates

The linear dependence of  $X$  on time indicates that the rate of monomer consumption during Stage II is of the first order in monomer concentration. Figure 8 shows that at all temperatures examined, this first order constant is proportional to the initiator concentration. From the gradient in Fig. 8 the values of the rate constant  $k$  in

$$-dM/dt = kC_0M \quad \dots \dots \dots (4)$$

have been derived, and collected in Table X. The Arrhenius plot, Fig. 9 (upper line) shows that the values derived from Stage II at the lower temperatures are consistent with values derived at  $0^\circ$  and  $25^\circ$ , from polymerizations in which no Stage I is apparent.

### 3.3.3 Effect of Perchlorate Salt, $nBu_4NClO_4 \equiv S$

Irrespective of whether it was added to the initiator or to the monomer solution, this salt caused a depression of both the Stage I conversions and the Stage II rates.

The effect on Stage I conversions was quantitatively similar to the effect on the total conversion at  $-97^\circ$  (Fig. 5). As illustrated in Fig. 10 (upper graph) for  $-71^\circ$  and  $-60^\circ$ , an inverse square root relationship is obeyed, indicating that  $X_1 \rightarrow 0$  as  $S \rightarrow \infty$ .

The effect on Stage II is quantitatively different. Quite small concentrations ( $S \sim C_0$ ) of salt cause marked reductions in rate (e.g. 3-fold) but larger doses do not have corresponding effects. Plots of  $k$  against  $S^{-2}$  (Fig. 10, lower graphs) seem

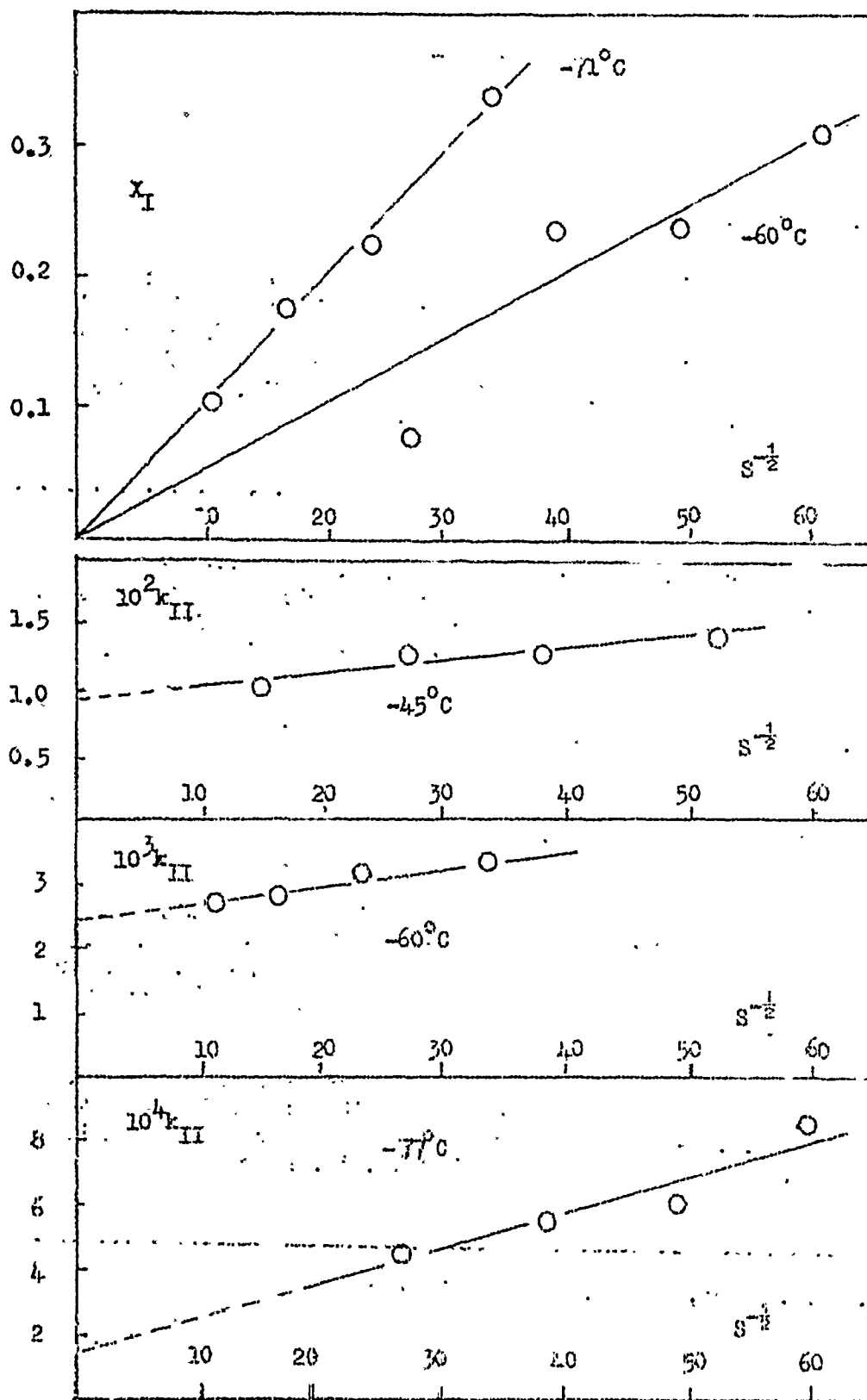


Fig. 10 Salt Effect on  $K_I$  (upper graph) and  $k_{II}$

definitely to extrapolate to an intercept at  $S^{-\frac{1}{2}} = 0$ , i.e. there appears to be a definite limiting value ( $k_{lim}$ ) below which the rate constant cannot be reduced by the suppressive action of the salt.  $k_{(lim)}$  then represents the rate constant of the reaction caused by non-suppressible species (e.g. ion pairs).

The values of  $\log k_{(lim)}$  are plotted in Fig. 9 and indicate that there is no great difference in the activation energies in the normal and in the salt-suppressed polymerizations.

### 3.3.4 Molecular Weights

Great pains were taken to ensure that the molecular weights were valid  $\bar{M}_n$ , suitable for use in kinetic deductions. Thus special precautions were taken to prevent any fractionation during isolation, and precipitation methods were not used. The samples were purified by freeze drying (twice if necessary) from the solvent, benzene, in which the VPO measurements were to be taken.

The  $\bar{M}_n$  values obtained are collected in tables IV - IX. They all lie in a rather narrow range (1000 - 9000), and at any one temperature may span almost the whole of this range, according to catalyst concentration and extent of conversion of the samples. Clear correlations do not leap to the eye, but can be disentangled by consideration of the derived quantity,  $n$  ( $\equiv 104(M_0/C_0)(Y/\bar{M}_n)$  - = number of polymer chains formed per initiator molecule) which indicates the degree to which transfer processes are operating. The following qualitative trends can be seen

(a) at low temperatures (e.g.  $-71^\circ$   $-60^\circ$ )  $\bar{M}_n$  are approximately inversely proportional to  $C_0$  and increase with conversion, the characteristic behaviour of a 'living polymerization'. The number  $n$  in Stage I (2 minute) samples is close to unity and increases slightly with conversion in Stage II.

(b)  $T \rightarrow 30^\circ$  to  $0^\circ$ .  $\bar{M}_n$  decreases with conversion and is only very weakly dependent on  $C_0$ .  $n$  rises with conversion to high values. This behaviour has previously been found in this and related polymerizations in ethylene dichloride at  $-30^\circ$ ,  $0^\circ$  and  $25^\circ$ .<sup>1,4)</sup>

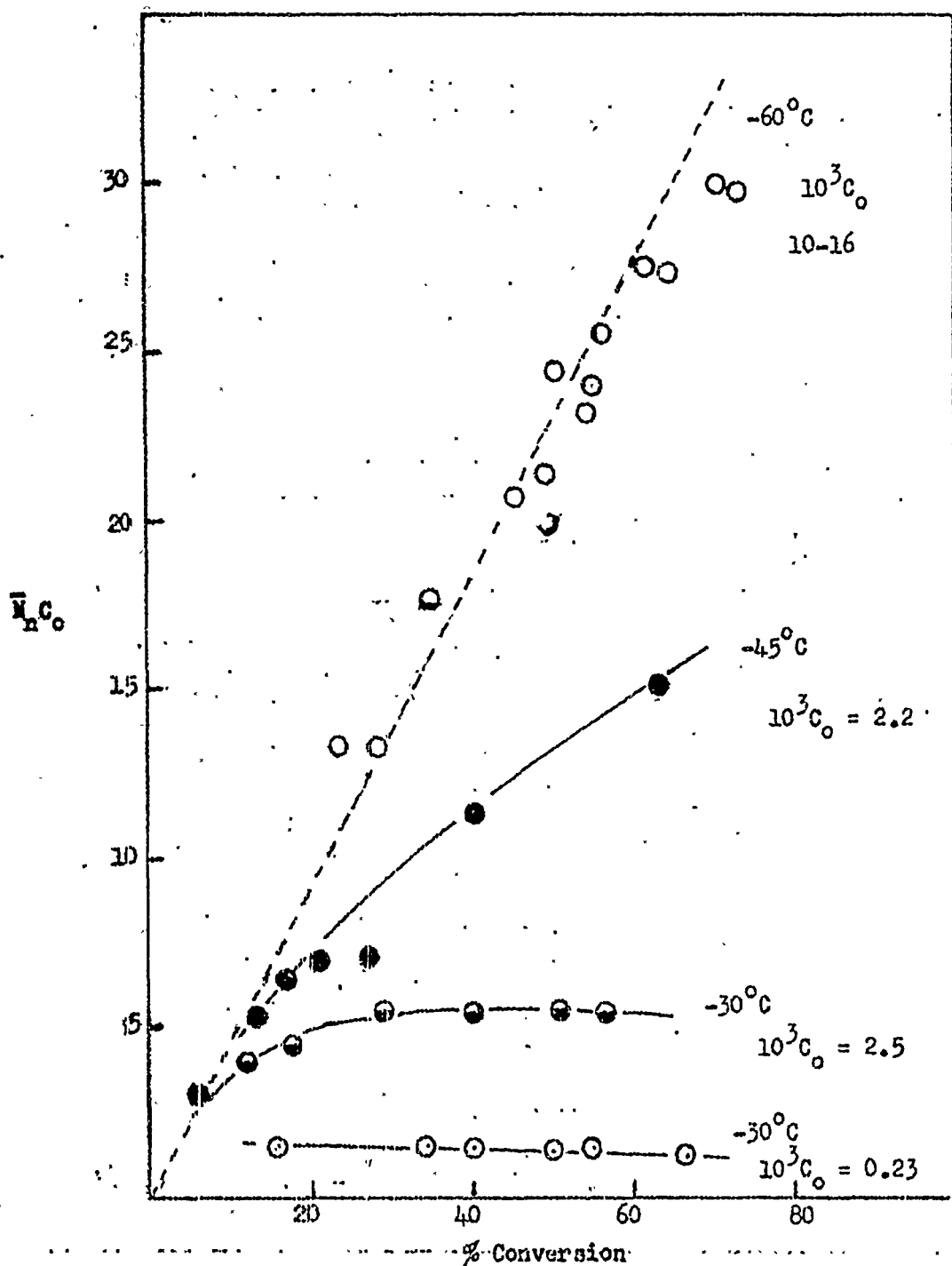


Fig. 11 Deviations from "Ideal"  $\bar{M}_n = 104(M_0/C_0)Y$

All at  $M_0 = 0.435$  m/l

(c) the perchlorate salt has little or no effect on the  $\bar{M}_n$ , provided they are compared at a given  $C_0$  and extent of conversion. The values of  $n$  appear to be distinctly smaller in salt-containing systems at low temperatures, but there is no significant difference at  $-30^\circ\text{C}$ .

The overall pattern is most clearly illustrated by a plot of the data from salt-containing systems in Fig. 11, in which the product  $\bar{M}_n \cdot C_0$  is plotted against the percentage conversion. For ideal 'living polymerizations', all points would be on a single line  $\bar{M}_n \cdot C_0 = 104 \bar{M}_0 \cdot Y$ . It can be seen that at  $-60^\circ$  all points (which include wide variations in  $C_0$  and in salt concentration) do lie close to the ideal line. At  $-45^\circ$  there are progressive deviations as the conversion rises. At  $-30^\circ$ , the ideal relationship does not hold at all, and at this temperature lines corresponding to different  $C_0$  are widely separated. Results from salt-free polymerizations would be below the lines at  $-60^\circ$  and  $-45^\circ$  but are virtually superimposed at  $-30^\circ$ .

In salt-free systems at  $-71^\circ$  and  $-60^\circ$ , small deviations can be seen even in the Stage I (2 minute) samples. Thus plots of  $\bar{P}_n$  against  $\bar{P}_n$  (ideal) (as Fig. 3 at  $-97^\circ$ ) give lines of slightly lower slope corresponding to  $n = 1.1$  at  $-71^\circ$  and  $1.2$  at  $-60^\circ$ . These  $n$  values then increase during the subsequent Stage II conversion.

The deviations are affected not only by the Stage II conversion but also by the initial catalyst concentration and at the higher temperatures, as shown in Fig. 12

$$n = A + k'' X_{II} / C_0 \quad \dots \dots \dots (5)$$

where  $k''$  is a constant increasing with temperature, and  $A$  has values close to unity at all temperatures - and can be identified with the small deviation from ideal behaviour occurring in Stage I. The results at  $-60^\circ$  and  $-71^\circ$  can also be represented by equation (5) though the Stage I conversions attainable at these temperatures, and the corresponding  $n$  values, are too small to be plotted on Fig. 12.

#### 3.4 Ordinary Temperatures, $0^\circ\text{C}$ and above

Molecular weights are very low ( $\bar{M}_n < 2000$ ) under all conditions studied. Values are listed in Table IX and their steep increase of  $n$  with conversion has been described in the last

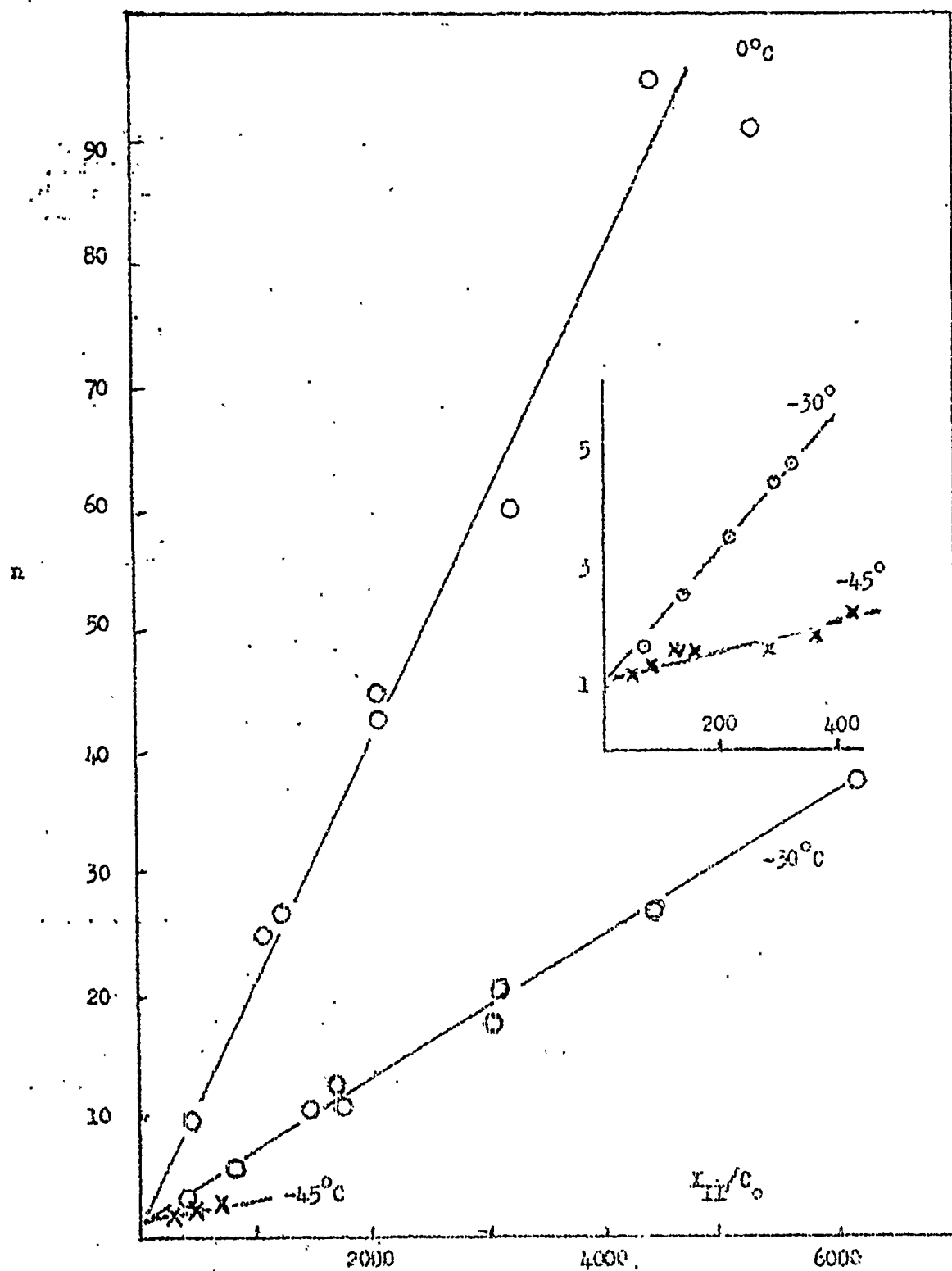


Fig. 1. Increase of  $n$  with conversion

section. The yields increase with reaction time in accordance with first order kinetics - i.e.  $X$  is linear with time (v. Fig. 1) showing no evidence of an initial, more rapid, Stage I. Similar behaviour was found by Darcy<sup>5)</sup> at 25°C in polymerizations followed dilatometrically. The derived rate constants are listed in Table X, and as mentioned in section 3.3.2 fit on the same Arrhenius line as the constants of Stage II rates at intermediate temperatures.

### 3.5 Molecular Weight Distributions

Three measurements of the weight average molecular weight  $\bar{M}_w$  were made on Stage I polymers (by light scattering) and indicate an unusually high  $\bar{M}_w/\bar{M}_n$  and hence broad distribution

Polymer	T°C	% Conv.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
D 70	-78	48	2920	67,000	23
D-122-3	-97	60	5500	115,000	21
D-122-8	-97	61	5400	85,000	16

This information is confirmed by the results of viscosity measurements. Fig. 13 shows that the intrinsic viscosity  $[\eta]$  relationship to  $\bar{M}_n$  for Stage I samples (open circles) lies well above the established relationship for sharp fractions in this range of  $\bar{M}_n$ . (ref. 5)

$$[\eta] = 1.0 \times 10^{-3} \bar{M}^{0.5} \dots \dots \dots (6)$$

If equation (6) is used as a basis for the calculation of the viscosity average  $\bar{M}_v$ , then  $\bar{M}_v/\bar{M}_n$  is found to have values 30-40 for all Stage I samples.

Another equation, probably more strictly applicable to the present samples, found by the same authors to hold for  $M > 50,000$ , is

$$[\eta] = 8.5 \times 10^{-5} \bar{M}^{0.75} \dots \dots \dots (7)$$

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5. Altares, Wyman & Allen, J. Pol.Sci. A2, 4533(1964)



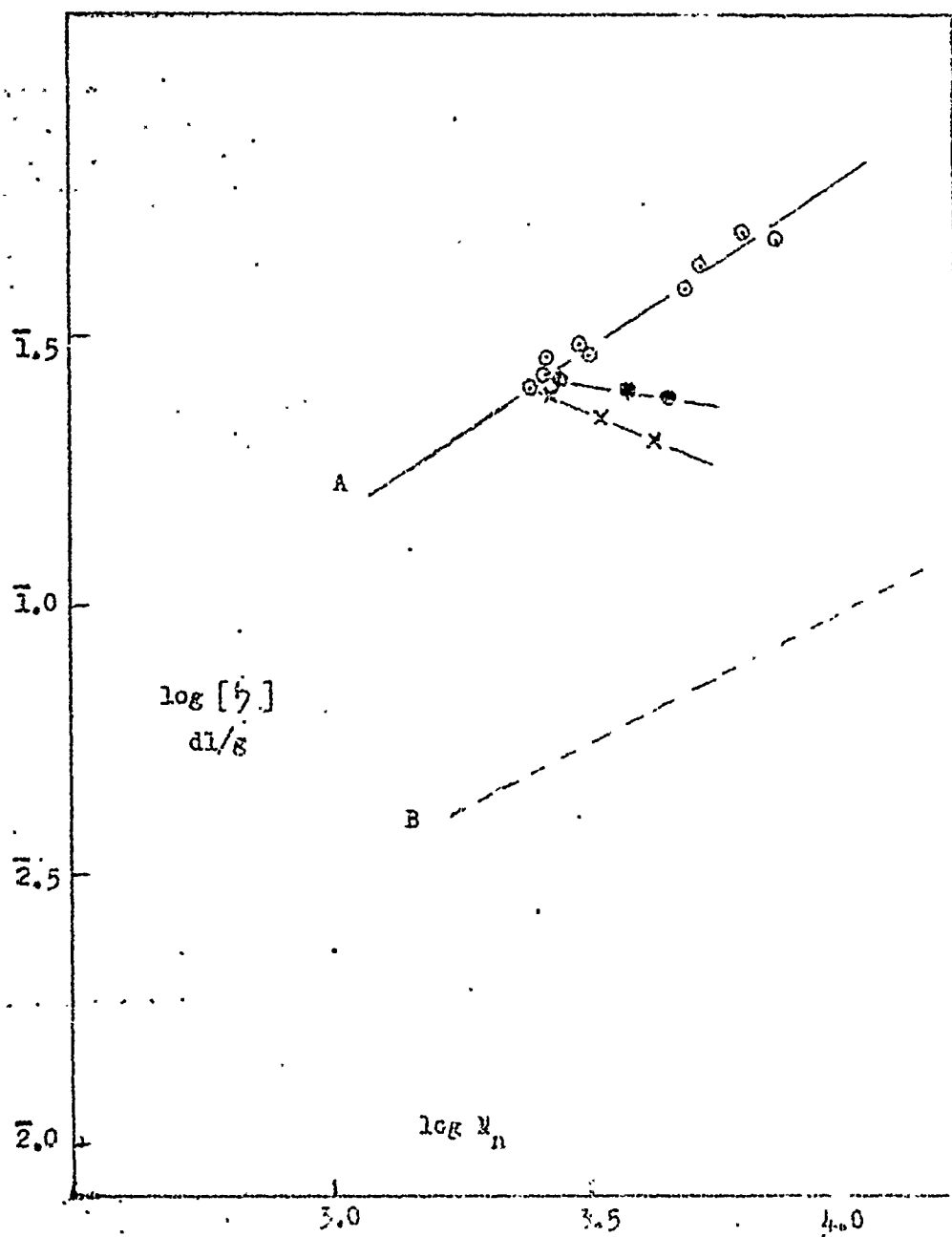


Fig. 13 Intrinsic Viscosities

A OOO Stage I samples

OOO Stage II " " -72°C

XXX Stage II S -60°C

B Line for sharp fractions

Values of  $\bar{M}_v$  calculated from equation (7) give  $\bar{M}_v/\bar{M}_n$  in the range 13-18. Neither calculation can be regarded as strictly quantitative, but it is evident that the distribution in Stage I polymers must be very broad.

In Stage II, however, the distribution becomes progressively narrower as conversion proceeds. This surprising conclusion is qualitatively evident from Fig. 13 where the intrinsic viscosity of Stage II samples at  $-71^\circ$  and  $-60^\circ$  (solid circles and crosses) is seen to fall with conversion, even though  $\bar{M}_n$  rises! The intrinsic viscosities of these samples yield  $\bar{M}_v$  (via equation (6) which give

at $-71^\circ$ , $\bar{M}_v/\bar{M}_n$	26	falling	with	increasing	conversion	to	13
$-60^\circ$	24		"		"		10

### 3.6 2:4:6 Trimethyl Styrene/ $\text{CH}_2\text{Cl}_2/\text{HClO}_4$ at $-97^\circ\text{C}$

Eight polymerizations of this monomer have been carried out in salt-free conditions and six in presence of  $\text{nBu}_4\text{FClO}_4$ . The reaction system is more complicated in that the polymer separates from solution at this temperature. Molecular weights are all very low ( $<1500$ ) and it is not yet known whether this is a true kinetic property of the polymerization or a consequence of polymer insolubility.

Within this limited study, this monomer behaves similarly to styrene, but with higher reactivity. Thus it shows a Stage I polymerization of similar magnitude ( $k' \sim 100$ , of styrene has  $k' 137$  at  $-97^\circ$ ), but a subsequent Stage II rate at  $-97^\circ$  equivalent to that of styrene at  $-45^\circ\text{C}$ . Salt suppresses the Stage I conversion and reduces the Stage II rate as in the styrene polymerization.

### 3.7 $\alpha$ Methyl Styrene/ $\text{CH}_2\text{Cl}_2/\text{HClO}_4$ at $-97^\circ\text{C}$

This monomer polymerizes very actively at  $-97^\circ$  with  $\text{HClO}_4$  concentrations ten times lower than used for styrene. Very viscous solutions are formed, indicating high molecular weights, and at high conversion some polymer precipitation occurs.

Both Stage I conversions and Stage II rates are observed at  $-97^\circ$ . The effect of salt has not yet been studied.

### 3.8. Dissociation Constants for $n\text{Bu}_4\text{NClO}_4$ in $\text{CH}_2\text{Cl}_2$

To evaluate the dissociation constant of this salt measurements of electrical conductance were made over a concentration range  $\sim 1 - 10 \times 10^{-6}$  g/l in  $\text{CH}_2\text{Cl}_2$ , at 5 temperatures in the range  $25^\circ$  to  $-75^\circ$ . Ancillary quantities, the dielectric constant and viscosity of the solvent were interpolated from literature values and the magnitudes of the limiting equivalent conductance,  $\Lambda_0$ , and the dissociation constant,  $K$ , were calculated by the methods of Fuoss. These values, and also "smoothed" values derived from the linear plot of  $\log K - 1/T$  are collected in Table XI.

### 3.9 Temperature Rise during Stage I at $-97^\circ\text{C}$

The rapidity of the 'flash' polymerization at  $-97^\circ$  and of Stage I at other temperatures must mean that this stage is almost adiabatic and a transient temperature rise is to be expected.

In reaction mixtures at  $-97^\circ$ , this temperature rise,  $\Delta T$ , (measured to  $\sim 0.2^\circ\text{C}$  by a thermistor probe coupled to a Chandos conductivity meter and recorder) was found to be as much as  $11^\circ\text{C}$  at the highest initiator concentration ( $\sim 10$  m.mol) which produced some 70% polymerization. At lower  $C_0$ , and conversion, approximately proportionate values of  $\Delta T$  were found. In all cases the peak occurred  $\sim 30$  seconds after mixing.

The identical time-scale for the  $\Delta T$  in the different reactions, and the knowledge that thermal contacts were poor leads to the belief that this time-scale is determined by heat transfer rather than by the heat evolution in the polymerization. It is hence believed that the bulk of the Stage I reaction is completed in  $\sim 30$  seconds in all cases.

This transient temperature rise inevitably introduces some ambiguity into the assignment of the observed conversion, and constant  $k$ , to the nominal reaction temperature. However no great importance need be attached to this question, in view of the relatively small temperature dependence of the  $k$  constant.

### 3.10 Colour and Conductance Observations

In none of the conventional experiments described above were any visible colours developed. Any electrical conductance was very small, e.g. at  $-97^{\circ}$  in polymerizations at  $M_0 = 0.43$ ,  $K \sim 10^{-8}$  mhos,  $\sim 20\%$  greater than that expected for  $\text{HClO}_4 \cdot \text{CH}_2\text{Cl}_2$  at the same concentration.

In such experiments the lowest ratio of monomer to initiator  $M_0/C_0$  was  $\sim 28$ . In a series of special experiments at  $-97^{\circ}$ , higher  $C_0$  and lower  $M_0$  were used giving  $M_0/C_0$  from 0.75 to 8. In all these systems a reddish colour developed on mixing and the conductance jumped up to 80 fold, both colour and conductance then remaining unchanged over many minutes at  $-97^{\circ}$ . On warming the solutions, the colour appeared unchanged and at room temperature was found to show the absorption spectrum (peaking at 420 n.m.) characterised by Bertoli and Plesch<sup>5)</sup> as that of a phenyl indanyl carbonium ion, formed in post-polymerization reactions. The formation of this species is known to require free  $\text{HClO}_4$ , liberated at the end of the polymerization at normal temperatures.

These low  $M_0/C_0$  systems were warmed from  $-97^{\circ}$  to  $-70^{\circ}$  and given a further dose of monomer to raise  $M_0$  to 0.435 (5% v/v). A slow polymerization was observed, at a rate corresponding to the normal Stage II reaction at this temperature. The colour and conductance changed in different ways according to the original ratio  $M_0/C_0$ . When this was  $< 1$  a further conductance jump occurred and the colour remained indefinitely. When  $M_0/C_0 > 2$  the conductance declined and the colour slowly faded with a time-scale of a few minutes, though the polymerization could be followed for hours.

The chief conclusion must be that the colour and conductance are not to be associated with the initiating or propagating species in the polymerization, but arise from subsequent reactions of polymer or oligomer when  $\text{HClO}_4$  is (perhaps only locally) in excess. The indanyl ion is capable of initiating further monomer, but does so only slowly at  $-70^{\circ}$ .

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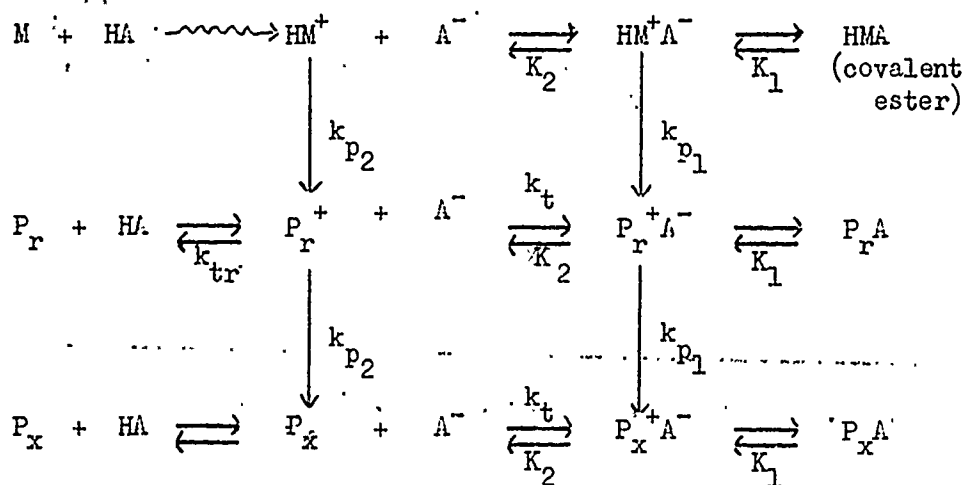
5. V. Bertoli & P.H. Plesch. Chem. Commun., 625 (1966)

#### 4. Interpretation and Discussion

The most important new features of the polymerization revealed by the foregoing experiments are

1. The extremely rapid and distinct initial stage noticeable at all temperatures below  $\sim -30^\circ$ , which becomes more important as the temperature is lowered until at  $-97^\circ$  it is the only observable reaction, having the characteristics of a terminated polymerization.
2. The suppressive action of the perchlorate salt, implying that the initial stage is propagated by free ions and the subsequent stage by two species, free ions and some non-suppressible species.
3. The growth of  $\bar{M}_n$  with conversion during Stage II at low and intermediate temperatures.
4. The increasing importance of transfer reactions above  $\sim -50^\circ\text{C}$  as revealed by  $n > 1$  and its growth with conversion.

These features may be co-ordinated and summarised in terms of the following kinetic scheme, which must however be regarded still as illustrative rather than definitive. Writing HA for initiator, M for styrene, and the ion-pair symbol  $P^+A^-$  to denote a propagating species unaffected by excess anion:



The acid-expulsion reactions (lower left) are effectively transfer reactions and must in principle be also possible from the ion-pair species.

The observed pattern of behaviour may be expected if all equilibria lie towards the righthand side, and more so the lower the temperature. Thus at  $-97^{\circ}$ , the ionization and dissociation constants  $K_1$  and  $K_2$  have negligible values, so that the only observable reaction is the irreversible movement from left to right and down, consuming all the initiator and producing a limited yield of polymer ester,  $P_xA$ , whose magnitude and chain length are determined by the ratio of the rates of propagation and termination.

At somewhat higher temperatures where the ionization processes are appreciable but transfer still negligible, a similar rapid initial stage must be expected but now followed by a slower polymerization. This reaction, initiated by ionization and dissociation of polymer ester, propagated by both ionic species and terminated by ion-recombination should have a stationary character, but because the termination reactions are reversible, any terminated chain can subsequently 'revive' and grow again, so that the polymerization as a whole is a 'living' polymerization. The molecular weight should therefore grow with conversion.

At higher temperatures still, when transfer rather than termination becomes the predominant chain-stopping reaction, this 'living' character will be lost, and the number of polymer chains grow and  $\bar{M}_n$  fall with conversion.

Quantitative interpretation of the results will not be attempted at this time, because detailed theoretical treatment of both Stage I and Stage II encounter ambiguities which have still not been resolved.

In Stage I, the time-scale and hence the rate determining factor in the ion-generation process is still not established. In the present 'preparative' experiments, Stage I is virtually complete in  $<2'$  (though a further 'creep' was sometimes observed for up to  $15'$  at  $-97^{\circ}C$ ). In some preliminary, rather crude, flow experiments, reaction was complete in  $10''$  and probably in  $<2''$ . The evidence from the salt effect implies that termination in Stage I is by ion-recombination and hence extremely fast (possibly diffusion controlled giving  $k_t \sim 10^8 - 10^9$ ). Hence unless the ion concentration is extremely low (and initiation correspondingly slow) the time-scale of Stage I should be extremely short.<sup>6)</sup> The conclusion must be that the first interpretation of Stage I as a fast-initiated non-stationary

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6. D.C. Pepper. Int. Symposium Macromolecular Chemistry, Tokyo 1966 Abstracts Vol. I, p.42

polymerization (with  $k_i \gg k_p$  and  $k_t$ ) cannot be valid, even for an ideal reaction system with instantaneous mixing, and certainly not for the relatively slowly-mixed systems examined here. In the present experiments it seems likely that Stage I is poorly defined kinetically, and that the rate of ion-generation may be controlled by the speed of mixing. Detailed interpretation must however be postponed until results have been checked in a rapid flow reaction system.

Stage II also presents difficulties of interpretation. As tentatively formulated in the scheme, the rates should be described by the equations governing the analogous anionic polymerizations carried by both free and paired ions, with an added complication that two ionization equilibria are involved. Thus the overall reaction rate constant,  $k$ , should be given in salt-free and salt-containing systems respectively, by

$$k = k_{p1} K_1 + k_{p2} K_1 \frac{1}{2} K_2 \frac{1}{2} C_o^{-\frac{1}{2}} \quad \dots \dots \dots (8)$$

and

$$k = k_{p1} K_1 + k_{p2} K_1 K_2 C_o / \sqrt{s} \frac{1}{2} S_o^{\frac{1}{2}} \quad \dots \dots \dots (9)$$

Equation (9) is borne out by the results (Fig. 10) and the limiting values ( $k(\text{lim})$ ) as  $S_o \rightarrow \infty$  can in principle be identified with the product  $k_{p1} K_1$ . Analysis cannot however proceed further, especially since the results in salt-free systems appear inconsistent, i.e. the rate constant  $k$  shows no significant variation with  $C_o$  as required by equation (8).

The necessity to allow for two propagation constants, and in principle also for two transfer constants, correspondingly complicates the quantitative theoretical interpretation of the molecular weights. In principle these can be formulated in terms of the various kinetic constants by making use of the simple identity

$$\bar{M}_n = 104 \bar{P}_n = 104 \Delta M / N$$

where  $N$  represents the total number of chains sharing monomer and in these reactions is equal to the number originally started by the initiator ( $C_o$ ) plus the total formed by transfer both in Stage I ( $N_I$ ) and in Stage II ( $N_{II}$ ). The argument is easily developed for

the case where only one species propagates and hence

$$N_I = C_0 \cdot k_{tr} / k_t \quad \dots \dots \dots (10)$$

$$\begin{aligned} N_{II} &= \int_{t_I}^t k_{tr} P^* = -(k_{tr}/k_p) \int_{M_I}^{M_t} dM/M \\ &= k_{tr}/k_p \cdot \ln(M_t/M_I) = k_{tr}/k_p X_{II} \quad \dots \dots \dots (11) \end{aligned}$$

$$\text{Hence } N = C_0 + N_I + N_{II} = C_0 (1 - k_{tr}/k_t) + k_{tr}/k_p X_{II} \quad \dots \dots \dots (12)$$

$$\text{and } \bar{P}_n = \Delta M / [C_0 (1 + k_{tr}/k_t) + (k_{tr}/k_p) X_{II}] \quad \dots \dots \dots (13)$$

$$\text{or } n = N/C_0 = (1 + k_{tr}/k_t) \cdot (k_{tr}/k_p) X_{II}/C_0 \quad \dots \dots \dots (14)$$

A simple expression for the case where two species propagate has not yet been derived. It is surprising therefore to find that the experimental results for salt-free systems (section 3.3.4) do fit equation (14) very well (Fig. 12). Theoretical values of  $\bar{P}_n$  at various conversions, calculated from equation (13) are shown on Fig. 14. They represent the generally observed behaviour very faithfully, i.e. show how the dependence of  $\bar{P}_n$  with conversion changes from the typical living polymer behaviour (when the first term in the denominator dominates (high  $C_0$  or low  $k_{tr}/k_p$ ) to that of a typical transfer-dominated stationary polymerization ( $\bar{P}_n$  falling with conversion) when  $C_0$  is low and  $k_{tr}/k_p$  appreciable. It is hoped that this obscure situation may be clarified by a more extended examination of the effect of salt on  $\bar{M}_n$ . The present results appear to indicate that at low temperature the salt has only a small effect and that it raises  $\bar{M}_n$  (at a given conversion) by decreasing the  $n$  values. The same effect is not shown in the small number of results at higher temperatures where  $n$  is large.



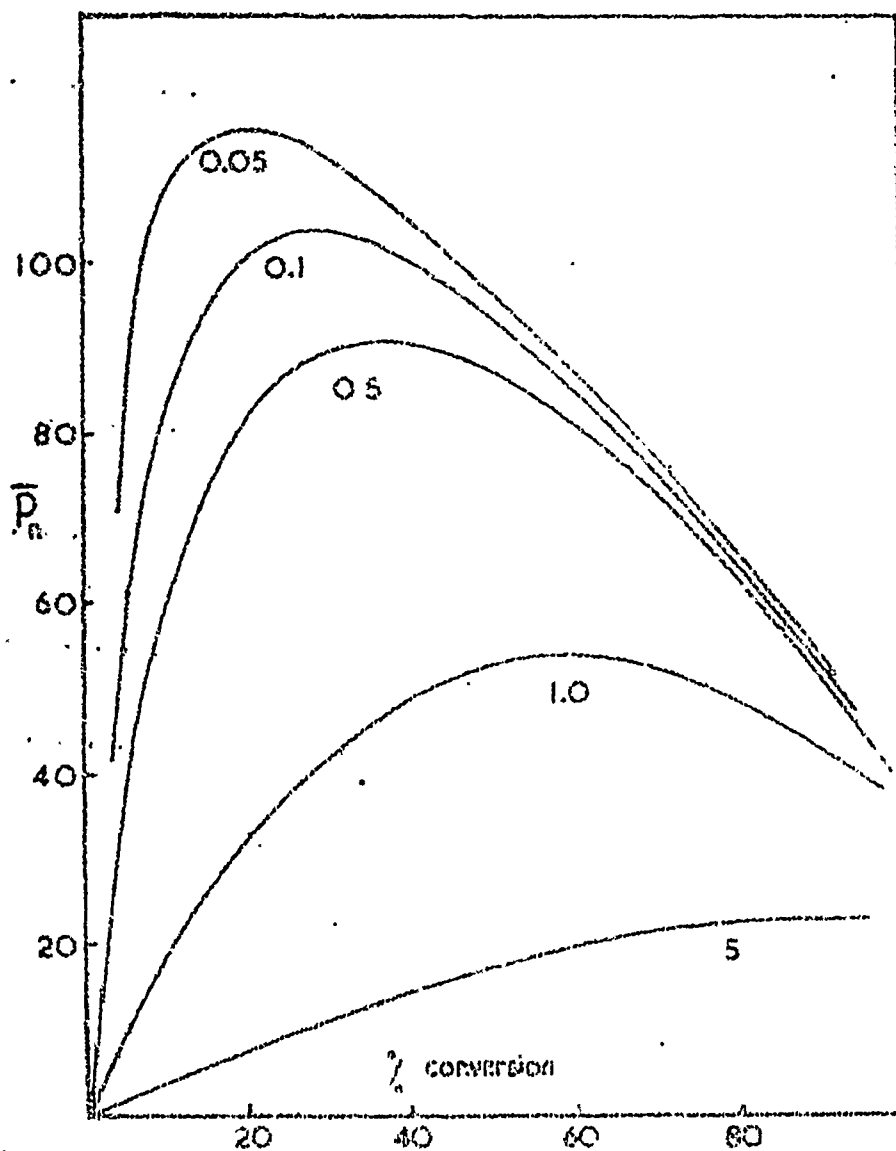


FIG. 11. THEORETICAL  $\bar{P}_n$  FOR  
 $M_0 = 0.43$   $k_1/k_2 = 1.0$   $k_3/k_4 = 3.10^9$   $C_2$  as shown

## 5. Conclusions

The research has reached a stage where the behaviour of the system over the whole practically accessible range of conditions has been sufficiently characterised so that it can be summed up in a few empirical equations. Consequently, a close practical control of the reaction is now possible, in that yields and molecular weights can be predicted for any chosen conditions.

One specific conclusion, which has important practical relevance, is that it will certainly not be possible to obtain really high molecular weights from styrene under any conditions with this catalyst. Thus at temperatures anywhere near room temperature, the molecular weights are severely limited by transfer. At much lower temperatures this limitation is avoided, but the controlling factor there is that the molecular weight must be inversely proportional to the initiator concentration. Thus high  $M_n$  requires very low  $C_0$  which makes for extremely low rates of conversion.

A clear insight has been gained into the overall kinetic pattern of the polymerization, and its relationship to the anionic polymerization seems now clear. The salt-effect has provided the first definite clue to the detailed nature of the propagating species. It has however not yet been possible to formulate a full kinetic scheme which is sufficiently explicit that quantitative derivations of fundamental rate constants can be made.

The future work necessary for further clarification clearly includes studies of the very fast initial Stage I by flow methods and a more systematic study of the effect of salt on molecular weights. Investigation of related monomers must also be extended to discover how far the kinetic behaviour revealed here for styrene is generally shared.

Table I

Effect of Perchloric Acid Concentration at  $-97^{\circ}\text{C}$

[Styrene] = 5% by volume; i.c. = 0.435 m/l

Expt. (1)	$10^3 C_0$ (2)	% Yield (3)	$X_I$ (4)	$X_I/C_0$ (5)	$\bar{M}_n$ (6)	$P_n$ (7)	$n$ (8)
39	0.9	8.0	0.083	92	5630	54.2	0.71
40	1.78	12.1	0.129	73			
90	2.6	32.0	0.390	151			
41	2.7	26.3	0.305	114			
42	3.6	36.9	0.461	128	5350	51.5	0.89
51	4.6	48.8	0.662	144	4780	46.0	0.98
86	5.0	47.0	0.635	127			
44	5.2	36.9	0.461	87			
45	6.1	46.5	0.625	103			
50	6.1	60.1	0.919	151	4300	41.4	1.03
46	7.1	62.5	0.981	138	3660	35.2	1.09
47	8.8	71.9	1.269	145	3360	32.3	1.10
81	9.7	74.0	1.347	139			
48	10.5	75.3	1.400	133	3100	29.8	1.05
49	12.1	80.2	1.620	134	2960	28.4	1.05
D107	3.5	53	0.755	215	7250	69.5	0.96
108	4.2	57	0.844	200	6250	60.1	0.99
110	5.6	63	0.944	168	5110	49.5	0.99
109	7.0	67	1.109	158	4800	46.2	0.88
112	7.2	71	1.238	172	4740	45.6	0.96

Table II

Effect of Styrene Concentration at -97°C

U indicates "uncompensated" systems - (variable  $\epsilon$ )

C " compensated " - ( $\epsilon \sim \text{constant}$ )

Expt. (1)	$M_o$ (2)	$10^3 C_o$ (3)	% Yield U (4) C (5)	$X_I/C_o$ U (6) C (7)	$M_n$ (8)	n (9)
53	0.174	4.6	66.5	238	3000	0.94
67	"	"	27.1	69		
52	"	6.1	77.6	240	2620	0.94
60	"	"	36.2	74		
51	0.435	4.6	48.8	144	4780	0.98
71	"	"	27.4	70	3040	0.94
50	"	6.1	60.1	151	4300	1.03
61	"	"	28.1	55	2390	0.87
74	0.87	4.5	38.0	107		
70	"	4.6	29.7	76	5640	1.07
54	"	6.1	47.7	106	7000	1.01
62	"	"	32.0	63	4800	0.99
75	1.22	4.6	33.5	92		
73	"	4.5	31.0	82	7850	1.11
56	"	6.1	36.1	74	6950	1.08
63	"	"	26.0	49	6100	0.96
72	1.74	4.5	26.8	71		
58	"	6.1	30.0	59	8250	1.07
65	"	"	27.1	52		

Table III

Effect of  $n\text{Bu}_4\text{NClO}_4$  at  $-97^\circ\text{C}$

All experiments at  $[\text{Styrene}] = 5\% \text{ v/v} = 0.435 \text{ n/l.}$

Expt. (1)	$10^3 C$ (2) $^\circ$	$10^3 S$ (3) $^\circ$	% Yield (4)	$X_I$ (5)	$\bar{M}_n$ (6)	n (7)
81	9.7	0	74.0	1.347	3180	1.08
82	9.6	0.159	49.5	0.683	2860	0.87
83	9.3	0.462	32.2	0.389	2040	0.77
85	9.1	0.745	22.6	0.256	1660	0.68
76	7.4	0	65.0	1.050	4140	0.97
79	7.3	0.161	34.2	0.419	2950	0.85
77	7.3	0.485	27.4	0.320	2530	0.67
78	6.9	0.760	17.7	0.195	1660	0.73
86	5.0	0	47.0	0.653	4870	0.90
87	4.9	0.164	20.6	0.230	2880	0.66
88	4.8	0.475	11.3	0.120	2520	0.43
89	4.7	0.770	8.1	0.085	2140	0.37
90	2.6	0	32.2	0.389	6300	0.90
91	2.5	0.167	9.3	0.098	3440	0.49
92	2.4	0.484	4.8	0.049	-	-
93	2.4	0.780	3.8	0.040	-	-

Table IV

Yields,  $\bar{M}_n$  and Salt Effects at  $-77^\circ\text{C}$

[Styrene] = 0.435

[ $\text{HClO}_4$ ] =  $8.4 \times 10^{-3}$

Expt.	$10^3 S_o$	t*	% Yield.	X	$\bar{M}_n$	n
17A	0	2	49.1	0.675	3500	0.76
17B	"	45	56.4	0.830	3640	0.83
17C	"	90	58.6	0.882	-	-
17D	"	120	60.7	0.934	4450	0.74
19A	0.28	2	27.1	0.316	1690	0.87
B	"	45	28.0	0.33	-	-
C	"	90	28.3	0.34	-	-
D	"	120	29.5	0.349	2180	0.93
21A	0.42	2	21.8	0.242	1570	0.74
B	"	45	23.2	0.264	-	-
C	"	90	24.3	0.278	-	-
D	"	120	24.6	0.282	-	-
18A	0.69	8	22.8	0.259	1600	0.77
B	"	45	23.5	0.268	-	-
C	"	90	24.6	0.282	-	-
D	"	120	24.6	0.282	1780	0.74
20A	1.38	2	6.25	0.064	-	-
B	"	60	10.6	0.112	-	-
C	"	120	12.8	0.137	900	0.76
D	"	220	9.7	0.101	-	-

\*Reaction time, minutes

Table V

Yields and  $\bar{M}_n$  at  $-71^\circ\text{C}$

[Styrene] = 0.435

[Salt] = 0

Expt.	$10^3 C_0$	$t^*$	% Yield	X	$\bar{M}_n$	n
D82A	1.4	45	14.5	0.155	4220	1.11
B	"	22	16.9	0.184	4330	1.25
C	"	180	23.3	0.263	4250	1.77
D	"	380	28.3	0.330	4490	2.06
D84A	3.9	2	32.0	0.356	3180	1.12
D85A	5.5	1	35.4	0.435	2650	1.16
B	"	4	36.5	0.452	2770	1.08
C	"	15	40.0	0.511	2740	1.20
D	"	150	57.0	0.843	3710	1.26
E	"	330	70.1	1.205	4400	1.30
D105	6.1	2	50.0	0.693	3380	1.11

\*t = Reaction time, minutes

Table VI

Yields and  $\bar{M}_n$  at  $-60^\circ\text{C}$

[Styrene] = 0.435 m/l.

Expt.	$10^3 C_0$	$10^3 C_n$	t	% Yield	X	$\bar{M}_n$	n
D87A	1.5	0	2	10.0	0.105	2580	1.16
B	"	"	10	13.2	0.140	2570	1.53
C	"	"	40	20.0	0.222	3570	1.68
D	"	"	105	31.7	0.380	3910	2.44
E	"	"	360	41.8	0.543	4710	2.67
D89A	4.3	0	2	26.2	0.303	2320	1.20
B	"	"	8	30.5	0.363	2610	1.23
C	"	"	60	43.7	0.575	3160	1.43
D	"	"	110	51.4	0.723	3310	1.63
E	"	"	410	79.8	1.600	4320	1.94
D96A	5.4	0	2	36.5	0.953	2460	1.25
B	"	"	30	50.6	0.702	2790	1.52
C	"	"	70	60.5	0.925	3080	1.66
D	"	"	120	68.5	1.55	3460	1.68
E	"	"	195	76.5	1.44	3600	1.74
31A	10.9	0.89	2	28.2	0.331	1210	0.97
B	"	"	60	36.1	0.448	1580	0.95
C	"	"	150	49.4	0.681	1804	1.13
32A	10.9	1.78	15	23.8	0.271	-	-
B	"	"	60	32.5	0.393	-	-
C	"	"	120	41.4	0.534	1720	1.00
D	"	"	210	55.6	0.810	2350	1.08
33A	10.9	3.5	17	17.0	0.186	992	0.70
B	"	"	62	23.6	0.269	1230	0.80
C	"	"	120	31.6	0.380	1450	0.93
D	"	"	178	38.3	0.483	-	-
34A	17.0	0.87	15	48.2	0.658	1260	1.02
B	"	"	60	57.5	0.858	1510	1.01
C	"	"	100	64.5	1.035	1620	1.06
D	"	"	150	72.9	1.306	1740	1.11
35A	17.0	1.73	22	45.0	0.598	1230	0.98
B	"	"	60	54.9	0.796	1400	1.03
C	"	"	120	62.3	1.00	-	-
36A	16.7	4.30	32	35.8	0.443	1070	0.91
B	"	"	92	50.0	0.693	1480	0.92
C	"	"	165	61.9	0.965	1660	1.01
D	"	"	223	70.3	1.214	1790	1.06
38A	16.1	8.2	15	15.0	0.160	-	-
B	"	"	60	27.6	0.322	-	-
C	"	"	120	40.5	0.520	-	-
D	"	"	240	61.0	0.940	-	-



Table VII

Yields,  $\bar{M}_n$  and Salt Effects at  $-45^\circ\text{C}$

[Styrene] = 5% v/v = 0.435 m/l.

Expt.	$10^3 C_0$	$10^3 S_0$	t	$\alpha$ Yield	X	$\bar{M}_n$	n
D130A	0.170	0	20	5.0	0.051	7500	1.6
B	"	"	30	7.1	0.073	8250	2.1
C	"	"	45	10.5	0.110	9250	2.9
22A	2.20	0	2	16.1	0.176	2780	1.14
B	"	"	45	41.0	0.538	4900	1.65
C	"	"	90	53.8	0.772	-	-
D	"	"	120	63.6	1.010	6550	1.91
24A	2.20	0.46	5	5.3	0.054	1170	0.89
B	"	"	45	11.6	0.123	-	-
C	"	"	90	17.2	0.189	-	-
23A	2.20	0.92	2	3.4	0.034	-	-
B	"	"	45	11.0	0.118	-	-
C	"	"	90	17.7	0.195	-	-
D	"	"	135	21.6	0.244	3030	1.40
25A	2.20	1.36	15	6.4	0.066	-	-
B	"	"	60	13.1	0.141	2280	1.13
C	"	"	90	17.5	0.192	-	-
D	"	"	150	26.9	0.313	3000	1.76
26A	2.2	4.5	15	3.2	0.032	-	-
B	"	"	60	5.4	0.055	-	-
C	"	"	90	7.0	0.072	-	-
D	"	"	150	9.1	0.096	-	-

Table VIII

Yields,  $\bar{M}_n$  and Salt Effects at  $-30^\circ\text{C}$

[Styrene] = 5% v/v = 0.435 m/l.

Expt.	$10^3 C_0$	$10^3 S_0$	t	% Yield	X	$\bar{M}_n$	n
D129A	0.18	0	110	27.2	0.317	6340	11
B	"	"	233	42.7	0.557	5880	18
C	"	"	388	55.6	0.810	5190	27
D	"	"	549	65.7	1.068	4520	36
D124A	0.23	0	79	18.5	0.205	6100	6
B	"	"	180	33.8	0.410	5090	13
C	"	"	330	51.1	0.715	4980	20
D	"	"	480	66.5	1.095	4170	31
D76A	1.25	0	12	16.7	0.182	2330	3
B	"	"	35	35.2	0.434	2870	4
C	"	"	55	49.0	0.673	2860	6
D	"	"	92	68.7	1.160	2830	9
D75A	2.5	0	6	24.2	0.277	2240	2
B	"	"	14	40.0	0.511	2640	2.7
C	"	"	26	55.4	0.809	2750	3.6
D	"	"	41	70.4	1.220	2610	4.9
E	"	"	60	81.4	1.685	2620	5.6
D73A	3.8	0	7	38.5	0.486	2960	1.7
B	"	"	12	51.8	0.730	2540	2.4
C	"	"	25	70.6	1.225	2720	3.1
D	"	"	40	84.6	1.866	2800	3.6
E	"	"	60	95.6	3.10	2680	4.5
27A	2.3	0.45	5	8.1	0.084	-	-
B	"	"	20	18.1	0.200	2100	1.7
C	"	"	40	29.8	0.354	-	-
D	"	"	60	39.5	0.503	-	-
28A	2.2	0.91	15	13.2	0.141	-	-
B	"	"	45	30.7	0.367	2300	2.62
C	"	"	75	45.0	0.598	-	-
D	"	"	105	56.7	0.837	2360	4.72
29A	2.2	2.3	15	10.4	0.110	-	-
B	"	"	45	24.5	0.281	-	-
C	"	"	90	41.5	0.538	2340	3.49
D	"	"	120	51.2	0.717	2300	4.38
30A	2.2	4.5	15	12.8	0.137	1620	1.56
B	"	"	45	27.3	0.319	-	-
C	"	"	90	45.0	0.598	-	-
D	"	"	120	55.0	0.797	-	-

Table IX

Yields and  $\bar{M}_n$  at 0°C

Expt.	$10^3 C_0$	t	% Yield	X	$\bar{M}_n$	n
D65A	0.09	25	16.7	0.182	1820	45
B	"	50	31.6	0.378	1680	95
C8	"	90	47.2	0.640	1620	145
D	"	155	65.2	1.056	1410	230
D58A	0.17	13	17.1	0.188	1760	25
B	"	55	59.1	0.845	1510	91
C	"	70	70.1	1.207	1360	139
D	"	152	86.4	1.995	1190	194
D64A	0.41	5	16.0	0.174	1830	10
B	"	15	39.5	0.501	1590	27
C	"	25	56.9	0.842	1460	43
D	"	40	72.7	1.298	1330	60
E	"	60	91.4	2.456	1140	88

Table X

Empirical Constants describing Conversions,  
Rates and Molecular Weights

Stage I conversion constants,  $k'$  (Sections 3.2.1, 3.3.1)

$T^{\circ}\text{C}$	-30	-45	-60	-71	-77	-97
$k' \text{ l m}^{-1}$	48	75	82	100	110	137

Stage II rate constants,  $k$  (Sections 3.3.2, 3.4)

$T^{\circ}\text{C}$	25	0	-30	-45	-60	-71	-77
$10^3 k \text{ l m}^{-1} \text{ s}^{-1}$	5800	1300	180	47	13	5.2	3.2
$10^3 k(\text{lim})$ "	-	-	43	10	2.7	-	0.2

Transfer-conversion constant  $k''$  (equation (5), section 3.3.4)

$T^{\circ}\text{C}$	0	-30	-45	-60	-71
$10^3 k'', \text{ ml}^{-1}$	20	6	2.5	(2.2*)	(1.1*)

\*estimated

Table XI

Dissociation of  $n\text{Bu}_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$

$T^\circ\text{C}$	$\eta$	$\epsilon$	$\Lambda_o'$	$\Lambda_o$	$\eta/\Lambda_o$	$10^5 K_d$
	(a)	(b)	(c)	(d)	(e)	(f)
25	0.414	9.00	124.3	119.3	4.94	2.85
0	0.535	10.02	96.4	92.7	4.96	6.92
-30	0.781	11.56	68.1	66.2	5.13	8.85
-45		12.42				(16.2)
-60		13.49				(25.1)
-61	1.237	13.51	39.1	39.53	4.89	29.5
-71		14.30				(36.3)
-75	1.531	14.60	29.0	28.53	4.37	37.4
-77		14.80				(45.7)
-97		15.65				(69.2)

(a) Viscosity in centipoise, calculated from Bingham equation  
for  $\eta = 1/\phi$ ,  $T^\circ\text{C} = 0.39806\phi + 212.97 - 2666.5/\phi$

(b) Dielectric constant, from J. Phys. Chem., 34, 2413 (1930)

(c) Limiting equivalent conductance, by extrapolation of  $\Lambda - C^{1/2}$

(d) Calculated from Fuoss plots . . . . .

(e) "Walden" product

(f) Dissociation constant (bracketed values interpolated  
from linear  $\log K_d - 1/T$  plot)

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13. ABSTRACT The report presents extensive measurements of number-average molecular weights ( $M_n$ ), yields and rates obtained in the polymerization of styrene by perchloric acid in solution in methylene chloride over the temperature range of 25°C to -97°C. The measurements show that the polymerization changes its kinetic pattern as the temperature is reduced and that the following well-defined characteristics can be recognized in different regions. At -97°C a 'flash' polymerization produces only a definitely limited yield of polymer, with $M_n$ corresponding to one chain per initiator, i.e. no transfer reactions are involved. At intermediate temperatures, e.g. -78°C to -30°C, a two-stage reaction occurs in which Stage I is similar to the above. Stage I is followed by Stage II, a stationary polymerization. Above -30°C a conventional transfer dominated stationary polymerization is obtained in which $M_n$ decreases with conversion and is virtually independent of initiator concentration. An inert perchlorate salt, $nBu_4NClO_4$ , causes severe reduction of the Stage I yields and partial reduction of the Stage II rates, indicating that free carbonium ions are the main propagating species in Stage I and two species act in Stage II.			

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